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SYNTHESIS OF CYCLOOCTATRIENE-1,4-DIONE BISETHYLENEKETAL

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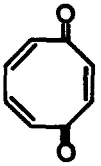
Recently, there has been considerable interest in the synthesis of the cyclooctatrienediones[1] and their valence tautomers.[2] We now wish to report the preparation of cyclooctatriene-1,4-dione bisethyleneketal (5), the immediate precursor of the potentially aromatic diketone (1).

Oxidation of 4-hydroxycyclooctanone[3] with chromium trioxide in aqueous acetic acid afforded the known cyclooctane-1,4-dione (2),[4] which was converted in 50% yield into the bisketal (3),[5] m.p. 40-43°, under carefully controlled



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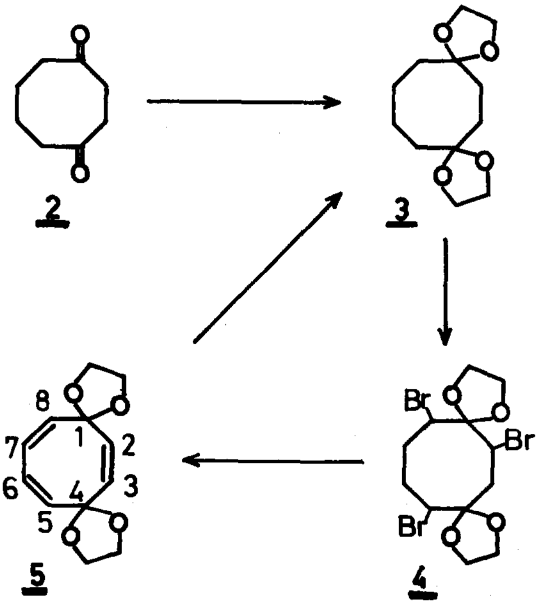

conditions (ethylene glycol, oxalic acid, and trimethyl orthoformate in acetonitrile for 12 hours at room temperature.)[6] Bromination of the bisketal (3) with three equivalents of bromine in ether at room temperature gave in 30% yield a crystalline tribromide (4),[5] m.p. 184-186°, which appeared to be a single compound, although the relative stereochemistry has not yet been defined. The spectral data for the intermediates (2)-(4) are shown in the Table.

Dehydrobromination of the tribromide (4) with potassium *t*-butoxide in refluxing *t*-butanol for seven days gave cyclooctatriene-1,4-dione bisethyleneketal (5),[5] m.p. 74-76°, in 50% yield. Dehydrobromination (90°, 3 days) in diazabicyclo[5.4.0]undec-5-ene (DBU) produced the triene bisketal (5) rather less efficiently (25%). Compound (5) showed a parent molecular ion in the mass spectrum at m/e 222.0898. $C_{12}H_{14}O_4$ requires m/e 222.0891. The monocyclic nature of this product was confirmed by its hydrogenation at atmospheric pressure (Pt/hexane) to the saturated bisketal (3), identical in all respects with an authentic sample.

The triene bisketal (5) showed essentially three signals in the ^1H n.m.r. spectrum of a carbon tetrachloride solution: τ 3.70 (s, 2H, $H_{2,3}$), 4.38 (s, 4H, $H_{5,6,7,8}$), 6.10 (finely split m, $\underline{W}_H$ 7 Hz, 8H, ketal CH_2). In perdeuterobenzene solution, solvent shifts were observed, and the ^1H n.m.r. resonances occurred at τ 3.18 (s, 2H, $H_{2,3}$), 4.16 and 4.54 (AA'BB' m, $J_{AB}\cong 12$ Hz, $H_{5,6,7,8}$), 6.48 (s, 8H, ketal CH_2). The noise decoupled FT^{13}C n.m.r. spectrum in deuterochloroform solution exhibited the following signals: δ (relative to TMS) 78.1 and 78.4 (ketal methylene carbons), 118.5 ($C_{1,4}$), 142.1 ($C_{2,3}$), 151.7 and 155.5 p.p.m. ($C_{5,8}$ and $C_{6,7}$). The assignments of resonances to the ketal methylene carbons and to $C_{1,4}$ and $C_{2,3}$ were confirmed by off-resonance and gated decoupling experiments, but it was not possible to distinguish the resonance due to $C_{5,8}$ from that due to $C_{6,7}$. In the infrared spectrum (carbon tetrachloride solution) the double bonds of the triene (5) were evident at 1615 cm^{-1} while bands at 1165, 1150, 1120, and 1015 cm^{-1} indicated the presence of the ethyleneketal groups. The ultraviolet spectrum (EtOH) of (5) exhibited a maximum at 244 nm (ε 6700). Related compounds, such as 5,7-dibromocycloocta-1,3-diene [238 nm (ε 5670)] and 5,8-dibromocycloocta-1,3-diene [240 nm (ε 6310)] show very similar behaviour.[7] The chemistry of the triene bisketal (5) is under active investigation.[8]

TABLE

Spectral data for compounds (2)-(4)

Compound	i.r. (cm^{-1})	Solvent	100 MHz ^1H n.m.r. (τ)	Solvent
(2)	1715	CCl_4	7.32 (s,4H); 7.59 (m,4H) 8.14 (m,4H)	$CDCl_3$
(3)	1135, 1120 1095, 1050	CCl_4	6.21 (fine d, 8H) 8.28 (s,6H); 8.36 (s,6H)	CCl_4
(4)	1115, 1110 1060	CCl_4	4.90 (m,1H); 5.30 (m,1H) 5.70 (s,4H); 5.94 (s,5H) 7.24 (m,2H); 7.60 (m,4H)	$CDCl_3$

NOTES AND REFERENCES

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Belfast, Northern Ireland.

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3. We thank BASF, Ludwigshafen, for a generous supply of this compound.
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8. The award of a Science Research Council Studentship (to P.A.C.) is gratefully acknowledged.
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